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(54) **Process for hydroxylating
aromatic hydrocarbons**

(57) A process for the hydroxylation of aromatic hydrocarbons by means of hydrogen peroxide, consisting of reacting the compounds in the presence of synthetic zeolites containing either, substituted or exchanged heteroatoms. The reaction is carried out in acetone at a temperature of between 80 and 120°C.

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SPECIFICATION

Process for hydroxylating aromatic hydrocarbons

5 This invention relates to a process for the hydroxylation of aromatic hydrocarbons.

The direct hydroxylation of aromatic hydrocarbons with hydrogen peroxide has been known for some time, and is carried out in the presence of a catalyst which is generally chosen from transition metals.

However, this reaction has certain drawbacks, including a low selectivity with respect to the hydrogen peroxide because of the partial decomposition thereof by the metal ions; a low selectivity with respect to the reacted hydrocarbon because of coupling reactions of intermediate organic radicals; and, in the particular case of phenol, the fact that the diphenols which are formed are more easily oxidisable than the phenol itself, resulting in an inevitable reduction in the extent of conversion.

In carrying out the reaction between an aromatic hydrocarbon and hydrogen peroxide, it is known to use an acid aluminosilicate which has been poisoned or partly modified by a rare earth (US-A-3580956).

Although improving the performance of the reaction, the use of this catalytic material does not however completely eliminate the production of considerable quantities of useless by-products, the presence of which negatively influences the final results and the economy of the entire process.

From GB-A-2083816, it is known to be possible to bond hydroxyl groups to aromatic nuclei by reacting the aromatic hydrocarbon concerned with hydrogen peroxide, with none of the aforesaid drawbacks, by carrying out the reaction in the presence of synthetic zeolites containing either substituted or exchanged heteroatoms. Zeolite materials which can be used in this process can be chosen from, for example, those described in GB-A-2024790 and GB-A-2078704, which describe synthetic materials comprising crystalline silica modified by the presence of elements which enter the crystalline silica lattice in place of silicon atoms. The modifying elements may be chosen from Cr, Be, Ti, V, Mn, Fe, Co, Zn, Rh, Ag, Sn, Sb and B. Also disclosed in GB-A-2024790 and GB-A-2078704 are methods for preparing these synthetic materials, and reference should be made thereto for the necessary details and for a better understanding of the structure of the material itself.

Returning to the hydroxylation process, as disclosed in GB-A-2083816, it is important to emphasise the great advantage which derives from the use of synthetic zeolites, this advantage consisting of the facility for guiding the reaction towards the formation of one product rather than other by simply choosing a determined modified zeolite. Thus, for example, in the case of phenol hydroxylation, there may be used a porous crystalline synthetic material formed from silicon and titanium oxides, such as disclosed in GB-A-2071071. The use of such a material enables a mixture of hydroquinone and pyrocatechol in a ratio equal to or greater than 1:1 to be obtained.

The reaction between the aromatic hydrocarbon and hydrogen peroxide is preferably carried out at a temperature of from 80 to 120°C, in the presence of the hydrocarbon either alone or with a solvent chosen from water, methanol, acetic acid isopropanol or acetonitrile. Examples of the aromatic hydrocarbon are phenol, toluene, anisole, xylenes, mesitylene, benzene, nitrobenzene, ethylbenzene and acetanilide.

75 According to the present invention, there is provided a process for the hydroxylation of an aromatic hydrocarbon, which comprises reacting the aromatic hydrocarbon and hydrogen peroxide in the presence of a synthetic zeolite containing substituted and/or exchanged heteroatoms, the reaction being carried out in the presence of acetone.

Thus, we have now found that by reacting the hydrocarbon concerned in the presence of acetone, e.g. as a solvent, it is possible to carry out the reaction using high feed ratios and with high yields. The quantity of heavy by-products is usually very low. The reaction is preferably carried out at a temperature of from 80 to 120°C, more preferably carried out at the reflux temperature.

90 Examples of the aromatic hydrocarbon are those listed above.

In preferred embodiments, the synthetic zeolite is as claimed in any of claims 1 to 15 and 45 of GB-A-2024790, or as claimed in any of claims 1, 2 and 32 of GB-B-2024790, or as claimed in any of claims 1 to 7 and 29 of GB-A-2078704, or as claimed in any of claims 1 to 6 and 28 of GB-B-2078704.

The invention will now be illustrated by the following Examples, in which the following terms are used:

$$\text{Feed ratio} = \frac{\text{Moles of H}_2\text{O}_2 \text{ fed}}{\text{Moles of phenol fed}} \times 100$$

$$\text{Phenol selectivity} = \frac{\text{Moles of diphenols formed}}{\text{Moles of phenol reacted}} \times 100$$

$$\text{H}_2\text{O}_2 \text{ yield} = \frac{\text{Moles of diphenols formed}}{\text{Moles of H}_2\text{O}_2 \text{ fed}} \times 100$$

$$\text{Phenol conversion} = \frac{\text{Moles of phenol reacted}}{\text{Moles of phenol fed}}$$

$$\text{Hydroquinone selectivity} = \frac{\text{Moles of hydroquinone}}{\text{Moles of diphenols}} \times 100$$

HMME = hydroquinone monomethylether

$$\text{Anisole yield} = \frac{\text{Moles of HMME formed} + \text{moles of guaiacol formed}}{\text{Moles of anisole reacted}} \times 100.$$

EXAMPLE 1

50g of phenol, 39g of acetone and 2.5g of catalyst were fed into a 250 cc flask. When the system reached a temperature of 80°C, 10 cc of 36% w/v H₂O₂ were added. The following results were obtained after two hours of reaction:

Phenol selectivity	96.25%
Phenol conversion	18.36%
H ₂ O ₂ yield	88.5%
Tarry by-product/tarry by-product + diphenols	4.2%
Hydroquinone selectivity	50%

EXAMPLE 2

The procedure of Example 1 was repeated, but 15 cc of 36% w/v H₂O₂ were added. The following results were obtained after two hours:

Phenol selectivity	95.45%
Phenol conversion	24.25%
H ₂ O ₂ yield	79.6%
Tarry by-product/tarry by-product + diphenols	5.1%
Hydroquinone selectivity	50%.

EXAMPLE 3

The procedure of Example 2 was repeated, but 20 cc of 36% w/v H₂O₂ were added. The following results were obtained after two hours:

Phenol selectivity	92.96%
Phenol conversion	31.28%
H ₂ O ₂ yield	73.9%
Tarry by-product/tarry by-product + diphenols	7.8%
Hydroquinone selectivity	50%.

EXAMPLE 4

The procedure of Example 3 was repeated, but 25 cc of 36% H₂O₂ were added. The following results are obtained after two hours:

Phenol selectivity	91.29%
H ₂ O ₂ yield	68.9%
Tarry by-product/tarry by-product + diphenols	9.7%
Hydroquinone selectivity	50%
Phenol conversion	36.64%.

EXAMPLE 5

The procedure of Example 4 was repeated, but 30 cc of 36% H₂O₂ were added. The following results were obtained after two hours:

Phenol selectivity	89.4%
H ₂ O ₂ yield	59.4%
Tarry by-product/tarry by-product + diphenols	12%
Hydroquinone selectivity	50%
Phenol conversion	37.76%.

EXAMPLE 6

30 cc of anisole, 70 cc of acetone and 3 g of catalyst were fed into a 250 cc flask fitted with a bulb condenser. When a temperature of 70°C was reached, 7.5 cc of 36% H₂O₂ were added in drops. The following results were obtained on termination of the reaction;

Product distribution: HMME.....	64%
Guaiacol.....	36%
H ₂ O ₂ yield.....	72.8%
Anisole conversion.....	22.7%
Tarry by-product/tarry by-product + phenol product	6.26%
Anisole yield.....	90.6%

EXAMPLE 7

The procedure of example 6 was repeated, but 10 cc of 36% H₂O₂ were added. The results are as follows:

Product distribution: HMME.....	64%
Guaiacol.....	36%
H ₂ O ₂ yield.....	70%
Anisole yield.....	86%
Anisole conversion.....	24%
Tarry by-product/tarry by-product + phenol product	11%.

The catalyst used in all of the above Examples is a titanium silicalite prepared as described in Example 1 of GB-A-2071071.

CLAIMS

- 5 1. A process for the hydroxylation of an aromatic hydrocarbon, which comprises reacting the aromatic hydrocarbon and hydrogen peroxide in the presence of a synthetic zeolite containing substituted and/or exchanged heteroatoms, the reaction being carried
- 10 out in the presence of acetone.
2. A process according to claim 1, wherein the aromatic hydrocarbon is phenol, toluene, anisole, a xylene, mesitylene, benzene, nitrobenzene, ethylbenzene, or acetanilide.
- 15 3. A process according to claim 1 or 2, wherein the reaction is carried out at a temperature of from 80 to 120°C.
4. A process according to claim 1, 2 or 3, wherein the synthetic zeolite is as claimed in any of claims 1
- 20 to 15 and 45 of GB-A-2024790, or as claimed in any of claims 1, 2 and 32 of GB-B-2024790.
5. A process according to claim 1, 2 or 3, wherein the synthetic zeolite is as claimed in any of claims 1 to 7 and 29 of GB-A-2078704, or as claimed in any of
- 25 claims 1 to 6 and 28 GB-B-2078704.
6. A process according to claim 1, 2 or 3, wherein the synthetic zeolite is as claimed in any of claims 1 to 5 and 27 of GB-A-2071071 or GB-B-2071071.
7. A process according to claim 1, substantially
- 30 as described in any of the foregoing Examples.
8. A hydroxylated aromatic hydrocarbon when produced by a process according to any of claims 1 to 7.